## DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to a porosity film and a manufacturing method for the same. It is related with a porosity film suitably used as a separator for cells etc. which are arranged between the anode negative electrodes of a cell and make these isolate in more detail, and a manufacturing method for the same.
[0002]
[Description of the Prior Art]In recent years, in order to correspond to the cordless making of electronic equipment, etc., it is lightweight as a cell, higher electromotive force and high energy are obtained, and, moreover, the lithium cell with little self-discharge attracts attention. Between the anode negative electrodes of this lithium cell, the separator is formed for the prevention from a short circuit of an anode negative electrode.
In order to secure the permeability of the ion between anode negative electrodes as this separator, the porosity film which has many fine holes is used.
The porosity film using polymeric polyolefin as a material of this porosity film is proposed variously.
[0003]For example, using as a separator minerals porous membrane with a thickness of 10-200 micrometers constituted from inorganic powder and/or an inorganic fiber by polyolefin system resin as a method of raising the short circuit-proof nature in an elevated temperature is indicated by JP,10-50287, A. In this gazette, titanium oxide, an aluminum oxide, potassium titanate, etc. are mentioned as inorganic powder, and, generally the spherical thru/or needlelike inorganic substance is mentioned.
[0004]Although making draw magnification of said minerals porous membrane into about 1 to 10 times is indicated, since draw magnification of this level is low, the film strength obtained is not enough. If draw magnification is further enlarged in order to raise film strength when the porosity film using spherical inorganic powder and needlelike inorganic fiber is used as a lithium cell separator, membranous permeability will fall too much and membrane resistance will fall. In this case, for example, when an external short circuit etc. arise, a high current flows in an instant, and the temperature inside a cell rises dramatically, but the shutdown function of a separator cannot act, either but is dramatically dangerous with an instant.
[0005]
[Problem(s) to be Solved by the Invention]Therefore, the purpose of this invention has micropore structure and a moderate void content, and film strength and its permeability (Gurley value) are high, and there are in providing the manufacturing method of the porosity film which prevents the short circuit between the anode negative electrodes in an elevated temperature, and this porosity film.

[0006]
[Means for Solving the Problem]Polyolefine in which weight average molecular weight contains ultrahigh-molecular-weight polyolefine more than $1x10^6$ as a result of inquiring wholeheartedly, in order that this invention persons may solve said technical problem, Knead a resin composition which consists of inorganic powder and/or an inorganic fiber containing an inorganic substance which has flat sheet structure, and it fabricates to a sheet shaped, By extending and solvent removing, a porosity film obtained had micropore structure and had a moderate void content, and film strength and permeability were high, found out preventing a short circuit between anode negative electrodes also in an elevated temperature, and reached this invention.
[0007]Namely, a gist of this invention, [1]Weight average molecular weight is a porosity film which consists of 30 to 85 % of the weight of polyolefines, inorganic powder, and/or 15 to 70 % of the weight of inorganic fibers containing ultrahigh-molecular-weight polyolefine more than $1x10^6$, In a porosity film and a row, wherein this inorganic powder and/or an inorganic fiber contain an inorganic substance which has flat sheet structure [2]Weight average molecular weight kneads a resin composition which consists of 5 to 25 % of the weight of total amounts and 75 to 95 % of the weight of solvents of inorganic powder and/or an inorganic fiber containing polyolefine containing ultrahigh-molecular-weight polyolefine more than $1x10^6$, and an inorganic substance which has flat sheet structure, and fabricates to a sheet shaped, It is related with a manufacturing method of a porosity film which has the process of performing extension and desolvation treatment.
[0008]
[Embodiment of the Invention]As for the polyolefine which can be used for this invention, weight average molecular weight contains the ultrahigh-molecular-weight polyolefine more than $1x10^6$.
[0009]As ultrahigh-molecular-weight polyolefine, a homopolymer, copolymers, such mixed material, etc. of olefins, such as ethylene, propylene, 1-butene, 4-methyl-1-pentene, and 1-hexene, are mentioned. In these, it is preferred to use ultra high molecular weight polyethylene which is excellent in a mechanical strength from a viewpoint of high-intensity-izing of a porosity film.
[0010]The weight average molecular weight of ultrahigh-molecular-weight polyolefine is more than $1x10^6$, and is more than $1.5x10^6$ preferably. From a viewpoint of obtaining an elevated temperature and high melt viscosity, as for the content in the polyolefine of ultrahigh-molecular-weight polyolefine, 30 % of the weight or more is preferred, and its 50 to 100 % of the weight is more preferred.
[0011]From a viewpoint of obtaining moderate permeability and the short circuit-proof nature in the outstanding elevated temperature, the content in the porosity film of polyolefine is 30 to 85 % of the weight, and is 50 to 80 % of the weight more preferably 40 to 80% of the weight.
[0012]The inorganic powder and the inorganic fiber which can be used for this invention contain the inorganic substance which has flat sheet structure. That is, the inorganic powder and the inorganic fiber which have flat sheet structure are used suitably.
[0013]In this specification, the degree of flatness calculated by the following formulas from the distance (minor axis b) between two parallel lines of the shortest interval which touches the outline, and the height (thickness t) of the flat surface which is parallel to the level surface and touches particles and a fiber surface indicates five or more things to be flat sheet structures in the top view of particles or textiles. The degree of flatness is preferred for especially seven or more inorganic substances also in the inorganic substance which has flat sheet structure in this invention. SEM observation can perform measurement of the minor axis b and thickness t, for example.

[0014]The degree of flatness = minor-axis b / thickness t [0015]In this invention, the pitch diameter of inorganic powder is 0.1-5 micrometers, and 0.01-1 micrometer of average textiles thickness and 0.5-10 micrometers of mean fiber length's thing are preferred for it as an inorganic fiber. By using the inorganic powder's and/or the inorganic fiber's which contain the inorganic substance's which has flat sheet structure's in this invention having one big feature, and using the inorganic substance which has this flat sheet structure, An elevated temperature and an inter-electrode short circuit are prevented efficiently, and film thickness is reduced, and permeability is kept high, and the outstanding effect of raising safety is revealed.
[0016]When the inorganic substance which has such flat sheet structure is used, even if draw magnification is made high in stretching treatment and it manufactures a porosity film, Although it has micropore structure and a moderate void content and neither film strength nor permeability is necessarily clear about the reason a porosity film with high short circuit-proof nature in an elevated temperature is obtained high moreover, For example, since a big opening which surround an inorganic substance will produce if it extends and the inorganic substance has flat sheet structure in this invention to contact with polyolefine becoming small, when a spherical or needlelike inorganic substance is used, Even if extended, a touch area with polyolefine is large, and it thinks for controlling increase of a communicating hole.
[0017]Especially if it is the inorganic powder and the inorganic fiber which have flat sheet structure as said inorganic substance, it will not be limited, but for example, it is an insulator and an inorganic material [ inertness / in the inside of a cell ] is preferred. Although not limited in particular, as the example Kaolinite, nacrite, Mica, such as serpentine, such as montmorillonite minerals, such as kaolin fellows clay, such as dickite, montmorillonite, and Zaw Kona Ito, and lizardite, illite, a sericite, and glauconite, a vermiculite, etc. are mentioned. Especially in these, kaolin fellows clay and mica are preferred. These inorganic substances may mix two or more sorts, and may be used.
[0018]Said inorganic powder of the inorganic substance which has flat sheet structure, and the content in an inorganic fiber are 60 to 100 % of the weight more preferably 50% of the weight or more. Inorganic powder and/or an inorganic fiber without flat sheet structure may be contained in order to unite heat resistance and permeability with the characteristic of a cell and to control them, but it is preferred to consider it as less than 50% of the weight of quantity into inorganic powder and an inorganic fiber. As inorganic powder and an inorganic fiber without flat sheet structure, globular forms, such as titanium oxide, potassium titanate, and an aluminum oxide, or a needlelike inorganic substance is mentioned.
[0019]From a viewpoint of the improvement in heat-resistant, and film strength, the content in inorganic powder and/or the porosity film of an inorganic fiber is 15 to 70 % of the weight, and is 30 to 60 % of the weight more preferably 20 to 60% of the weight.
[0020]10-100 micrometers of thickness of the porosity film of this invention which consists of polyolefine, inorganic powder, and/or an inorganic fiber are 15-50 micrometers more preferably from a viewpoint [ make increase of the capacity of a cell easy and ] of securing film strength.
[0021]The void content of a porosity film is 40 to 70% more preferably not less than 40%. In particular, since the porosity film of this invention has the same micropore structure as the porosity film which consists only of polyolefines in addition to the void content of this range, the outstanding effect of having the outstanding electrolysis solution holdout is revealed.
[0022]The permeability of a porosity film prevents a high current flowing in an instant at the time of an external short circuit, 100 to 1500 sec/100 cc is 100 to 1000 sec/100cc more preferably from a viewpoint

[ make moderate the viewpoint and membrane resistance which secure the safety of a cell, and ] of performing rapid charge and discharge efficiently.
[0023]As for the film strength of a porosity film, it is preferred that the viewpoint of preventing the amniorrhexis of the film at the time of a cell assembly to **** intensity is 700 gf(s)/not less than 25 micrometers, and it is more preferred that it is 800 gf/not less than 25 micrometers.
[0024]It is preferred that the temperature which produces a short circuit is not less than 180 ** as short circuit-proof nature in the elevated temperature of a porosity film, for example, and it is more preferred that it is not less than 190 **.
[0025]The porosity film of this invention can be manufactured by mixing polyolefine, inorganic powder, and/or an inorganic fiber with a solvent, preparing a resin composition for example, kneading this, fabricating to a sheet shaped, and carrying out extension and desolvation treatment.
[0026]As amount of polyolefine, inorganic powder, and/or the inorganic fiber used, it is preferred in a resin composition in the total amount that it is 5 to 25 % of the weight, and it is more preferred that it is 10 to 25 % of the weight. The rate of a compounding ratio of the inorganic substance which has the flat sheet structure in the polyolefine in preparation of a resin composition, inorganic powder and/or the rate of a compounding ratio of an inorganic fiber, inorganic powder, and/or an inorganic fiber is suitably chosen so that each ingredient ratio which constitutes the porosity film obtained may serve as the range of the request specified by this invention.
[0027]That what is necessary is just what dissolves polyolefine as a solvent. For example, the mineral oil fraction corresponding to these in aliphatic series, such as nonane, Deccan, an undecane, a dodecane, a decalin, and a liquid paraffin, annular hydrocarbon, or the boiling point is mentioned, and non volatile solvents, such as a liquid paraffin, are preferred in these.
[0028]As amount of the solvent used, kneading torque, rolling, and extension stress are low respectively, and it is preferred that it is 75 to 95 % of the weight from a viewpoint [ make small the viewpoint which obtains the outstanding productivity, and the neck in at the time of sheet-izing, and ] of raising productivity to, in a resin composition.
[0029]To a resin composition, additive agents, such as an antioxidant and an ultraviolet ray absorbent, can be added in the range which does not spoil the purpose if needed.
[0030]The process which kneads the obtained resin composition and is fabricated to a sheet shaped can be performed by the publicly known method usually used. For example, using a Banbury mixer, a kneader, etc., it may knead, and a resin composition may be put between the metal plate ranked second and cooled, may be quenched by a batch type, it may be made a sheet-shaped molded product by quenching crystallization, and a sheet-shaped molded product may be obtained using the extrusion machine etc. which attached the T die etc.
[0031]The temperature in the case of kneading of a resin composition has the preferred range of temperature (dissolution starting temperature) -+60 ** which this solvent makes start the dissolution for the viewpoint [ distribute polyolefine efficiently and ] of suppressing disassembly of polyolefine to this polyolefine, and is more preferred. [ of the range which is the dissolution starting temperature of +20 ** - +50 ** ]
[0032]It faces fabricating to a sheet shaped and the sheet-shaped molded product which comes out from an extrusion machine etc. may be quenched further. At this time, it is more preferred that a supercooling degree (deltaT) quenches on the conditions which will be not less than 20 **.
[0033]Thus, the sheet-shaped molded product of a resin composition can be obtained. Here, although not

limited especially as thickness of a sheet-shaped molded product, a 1-20-mm thing is preferred, and what is 3-15 mm is more preferred.

[0034]Next, extension and desolvation treatment of a sheet-shaped molded product are performed. The method in particular of stretching treatment is not limited, may be the combination of the usual rolling method (the pressing method), the tenter method, the rolling method, tubular film processes, or these methods, and can apply any methods, such as uniaxial stretching and biaxial stretching. In the case of biaxial stretching, any of in-every-direction simultaneous extension or one by one extension may be sufficient. In this invention, rolling of a sheet-shaped molded product, etc. may be processed in advance of stretching treatment.

[0035]The temperature of stretching treatment has the good homogeneity of extension, and is preferred. [ of less than melting point (Tm)+5 ** of a viewpoint to polyolefine that obtains sufficient film strength ] 25 to 400 times of draw magnification are preferred, and its 50 to 300 times are more preferred. The publicly known conditions usually used can be used for other stretching treatment conditions.

[0036]Desolvation treatment is a process which removes a solvent from a sheet-shaped molded product and in which porous structure is made to form, for example, can be performed by removing the solvent which washes a sheet-shaped molded product with a solvent, and remains. As a solvent, hydrocarbon, such as pentane, hexane, heptane, and Deccan, Easy-volatility solvents, such as ether, such as hydrocarbon fluoridation, such as chlorine hydrocarbon, such as a methylene chloride and a carbon tetrachloride, and ethanetrifluoride, diethylether, and dioxane, are mentioned, and these can mix and use independent or two sorts or more. The method of the cleaning method in particular using this solvent not being limited, for example, a sheet-shaped molded product being immersed into a solvent, and extracting a solvent, the method of carrying out the shower of the solvent to a sheet-shaped molded product, etc. are mentioned.

[0037]What is necessary is just to perform desolvation treatment suitably before and after extension in this invention. For example, after carrying out desolvation treatment of said sheet-shaped molded product, stretching treatment may be presented, and desolvation treatment may be performed after carrying out stretching treatment of the sheet-shaped molded product as it is. Or it may be a mode which performs desolvation treatment before stretching treatment, performs desolvation treatment again after stretching treatment, and removes a residual solvent.

[0038]Heat setting processing of the molded product which has the porous structure acquired by said process can be carried out. In this invention, the heat setting processing can control the dimensional change of a film, and can use publicly known methods, such as letting it pass to a continuation hot blast stove. More than Tm-20 ** of polyolefine and less than Tm+5 ** of the temperature of heat setting processing are preferred. Although heat setting processing time changes with temperature and cannot generally be limited, it is preferred to carry out for 30 seconds - about 1 hour, for example.

[0039]In this invention, after preheating beforehand at the temperature not more than melting point-20 ** of ultrahigh-molecular-weight polyolefine, heat setting processing may be performed.

[0040]Thus, the porosity film of this invention obtained, It has micropore structure and a moderate void content, film strength and permeability are high, and since the short circuit-proof nature in the elevated temperature is excellent, it can be used conveniently not only for the use as a separator of a cell but the barrier membrane for various filters and electrolytic condensers, etc.

[0041]

[Example]Although an example and a comparative example are given and this invention is explained still in detail hereafter, this invention is not limited at all by this example. About the various characteristics, it measures in the following way.

[0042](1) Clip the porosity film of a void content measuring object to a round form 6 cm in diameter, and calculate using a following formula from the result obtained by finding the volume and weight.

[0043]Void content (%) =100x [The volume ($cm^3$)-weight (g) / mean density ($g/cm^3$)] /volume ($cm^3$)
The "mean density" in a formula is the mean density of polyolefine and inorganic powder, and/or an inorganic fiber.

[0044](2) Permeability (Gurley value)
It measures based on JIS P8117.

[0045](3) Heat resistance (short circuit-proof nature in an elevated temperature)
The size phi14mm anode which carried out dry immobilization after applying to a stainless mesh the paste which consists of $LiCoO_2$ and carbon black with a mean particle diameter of 10 micrometers, and a binder, The porosity film of the size beyond phi20mm is pinched with the size phi16mm negative electrode which carried out dry immobilization after applying to a stainless mesh the paste which consists of a carbon flake with a mean particle diameter of 10 micrometers and a binder, It inserts into a stainless plate via a tetrafluoroethylene sheet, and a torque wrench fastens the bolt of four corners with the torque of 1.0 kgf-cm, the conductivity of two poles is investigated with a tester, carrying out temperature up by 10 ** / min, and the temperature which produced the short circuit is measured.

[0046](4) Film strength (**** intensity)
**** intensity examined by carrying out a needle thrust prickle using the compression testing machine made from KATO Tech "KES-G5", from the load variation curve obtained by measurement, read maximum load and made it the **** intensity value. a needle uses 1.0 mm in diameter, and the tip curvature radius of 0.5 mm -- thrusting -- it carried out at 2 mm/second in speed.

[0047]Example 1 weight average molecular weight is ultra high molecular weight polyethylene (Tm: 133 **) of $2x10^6$. 3density 0.94 $g/cm^3$15 weight section, mica (pitch-diameter [ of 2 micrometers ] and density 2.6$g/cm^3$, degree 15 of flatness) 10 weight section, and liquid paraffin 85 weight section were mixed homogenously to slurry form, and dissolution kneading was carried out for 60 minutes using the small kneader at the temperature of 160 **. Then, such kneaded material was put between the metal plate cooled by 0 **, and it quenched to the 5-mm-thick sheet shaped. Heat pressing (one 6.1 times the draw magnification of this) of these sheet-shaped resin that carried out quenching crystallization was carried out until sheet thickness was set to 0.8 mm at 120 **, biaxial stretching was simultaneously carried out in all directions [ 3.5x3.5 times as many ] at 120 ** (one 75 times the total draw magnification of this), and desolvation treatment was performed using heptane. Subsequently, heat setting processing was carried out for 10 minutes at 130 **, and the porosity film which has 27 micrometers of thickness and the micropore structure of 57% of a void content was obtained.

[0048]Except not adding comparative example 1 mica, the film was produced like Example 1, deliquoring and heat setting processing were performed, and 25 micrometers of thickness and the porosity film of 52% of the void content were obtained.

[0049]It is potassium titanate (fibrous and 0.1 micrometer of average textiles thickness) instead of comparative example 2 mica. /$cm^3$, and degree of flatness 35 weight section, the film e performed, and 28 micrometers of thickness and the erature, and **** intensity of the porosity film obtained

| | 膜厚 [μm] | 空孔率 [%] | ガーレ値 [sec/100cc] | 短絡温度 [℃] | 突刺強度 [gf/25μm] |
|---|---|---|---|---|---|
| 実施例1 | 27 | 57 | 170 | 202 | 810 |
| 比較例1 | 25 | 52 | 138 | 163 | 870 |
| 比較例2 | 28 | 67 | 83 | 180 | 830 |

[0052]The porosity film obtained in Example 1 has a moderate void content compared with the porosity film obtained by the comparative examples 1-2, the Gurley value (permeability) and film strength are high, and the above result shows excelling in heat resistance (short circuit-proof nature in an elevated temperature).

[0053]

[Effect of the Invention]The effect that a porosity film with electrolysis solution solution retention have a moderate void content, and film strength and permeability are high, high the short circuit-proof nature in an elevated temperature and sufficient can be obtained by this invention is done so. The porosity film of this invention can be used conveniently not only for the use as a battery separator but the barrier membrane for various filters and electrolytic condensers, etc.

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## (54) POROUS FILM AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a porous film which has a microfine porous structure and an appropriate porosity and are high in membrane strength an air permeability (Gurley value) and prevents short circuit between the positive and negative electrodes at a high temperature, and a process for producing the same.

SOLUTION: The porous film is composed of 30-85 wt.% polyolefin containing an ultra-high-molecular-weight polyolefin having a weight average molecular weight of nor smaller than 1×106 and 15-70 wt.% inorganic powder and/or inorganic fibers, and the inorganic powder and/or inorganic fibers comprise as inorganic material having a plate structure. A process for producing porous films comprises the steps of kneading a resin composition composed of 5-25 wt.% polyolefin and inorganic powder and/or inorganic fibers containing an inorganic material having a plate structure in total and 75-95 wt.% solvent, molding the composition into the form of a sheet and effecting stretching and desolvation treatment.